



# ENABLING HIGH-ENERGY/HIGH-VOLTAGE LITHIUM-ION CELLS FOR TRANSPORTATION: PROJECT COMPLETION HIGHLIGHTS, PART 2

Project ID: BAT253

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Annual Merit Review

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# Overview

## Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 100%

## Budget

- Total project funding:  
FY18 \$4.0M
- BAT252, BAT253(ANL, NREL, ORNL, LBNL)

## Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety

## Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

# Project Objectives - Relevance

**Energy and Power loss during calendar-life and cycle-life aging limits the commercial viability of lithium-ion cells for transportation applications**

- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing layered-oxide-based positive electrodes
- To achieve the energy and power density targets, cells with these electrodes must be cycled to voltages that exceed 4.5 V vs. Li/Li<sup>+</sup>
- On extended cycling at these voltages, capacity loss, impedance rise and voltage fade reduce the cell's energy and power output
- Our goal is to examine the mechanisms associated with this loss in performance and to develop cell chemistries that enable operation over the 15 y life target set by the DOE-OVT

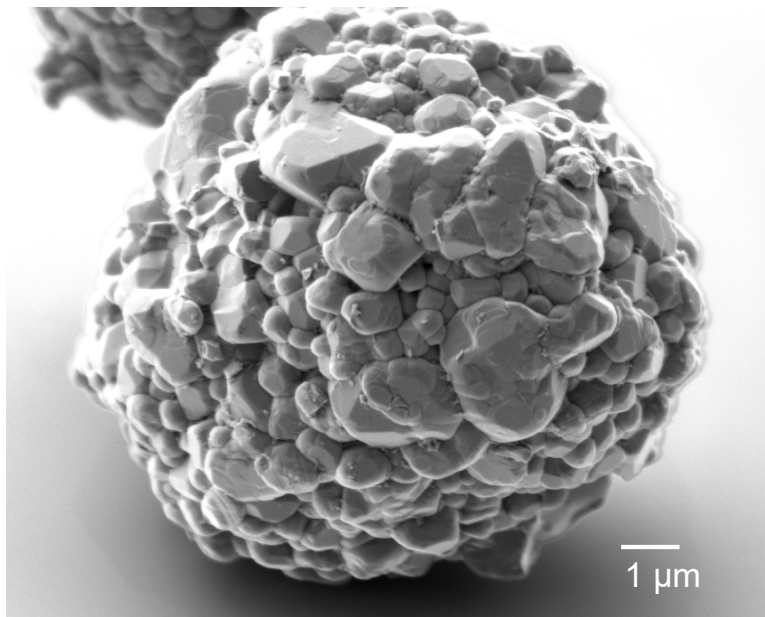
# Approach

## Multi-institutional effort to identify and solve performance loss problems in the high energy high voltage cells

- Determine factors that contribute to performance decline (capacity fade, impedance rise) in cells with layered-oxide (positive) and graphite (negative) electrodes
  - Develop/use diagnostic tools and techniques to identify cell constituents and reaction mechanisms associated with this performance loss
- Identify additives, which when incorporated into our baseline electrolyte (Gen2), consisting of 1.2M LiPF<sub>6</sub> in EC:EMC (3:7 w/w), reduces cell degradation
  - Provide an understanding of electrolyte-additive mechanisms through closely-coupled experimental and computational techniques
- Identify novel electrolyte systems that outperform the baseline Gen2 electrolyte
  - Examine fluorinated electrolytes which are known for high-voltage stability
- Develop test protocols to examine oxidative stability of electrolytes
  - Investigate and model the parasitic currents observed at high cell voltages
- Formulate experiments to examine the various crosstalk processes during cycling
  - Identify effects of transition metals and gas generation on cell performance
- Report/publish experimental data to advance understanding of HE/HV cells
  - Document approaches/methodologies in presentations and publications

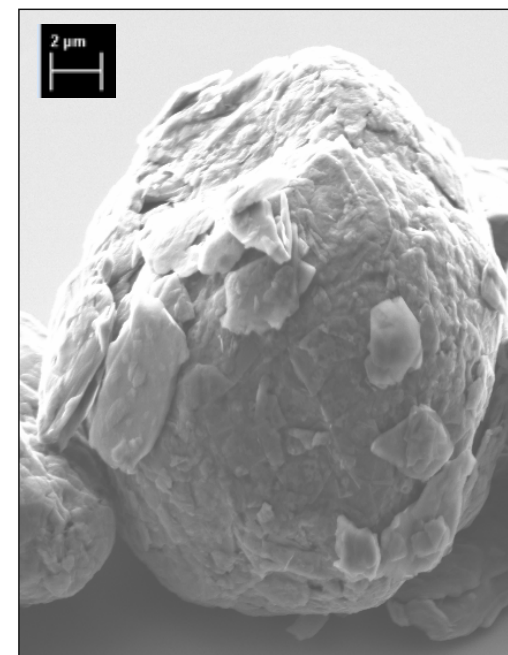
# Electrodes fabricated at the CAMP facility are used for various tests

Baseline Chemistry: NMC532 positive & graphite negative electrodes



Baseline Electrolyte

- 1.2 M  $\text{LiPF}_6$  in EC/EMC (3:7)



Positive Electrode contains

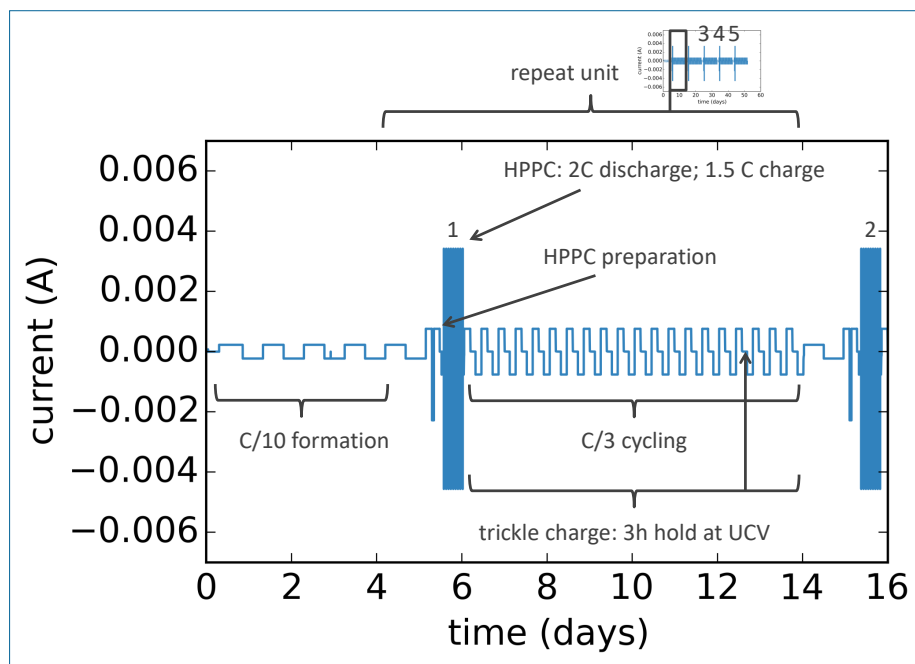
- 90 wt% NMC532 Oxide
- 5 wt% C45 carbon
- 5 wt% PVdF binder

Negative Electrode contains

- 92 wt% A12 Graphite
- 2 wt% C45 carbon
- 6 wt% PVdF binder

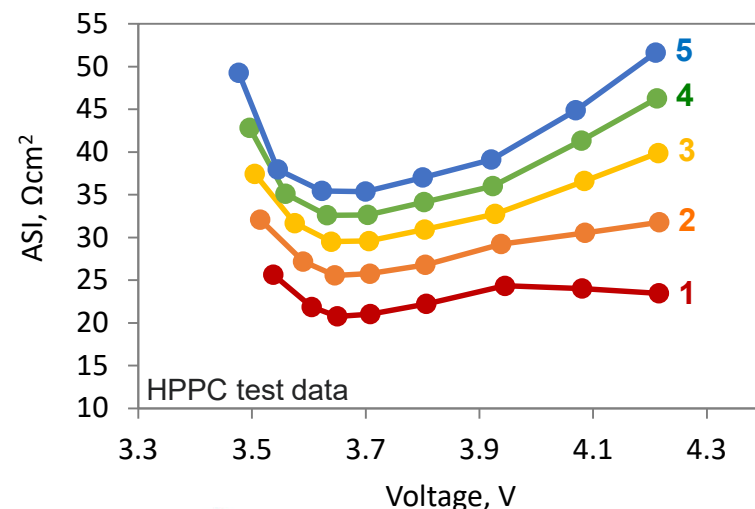
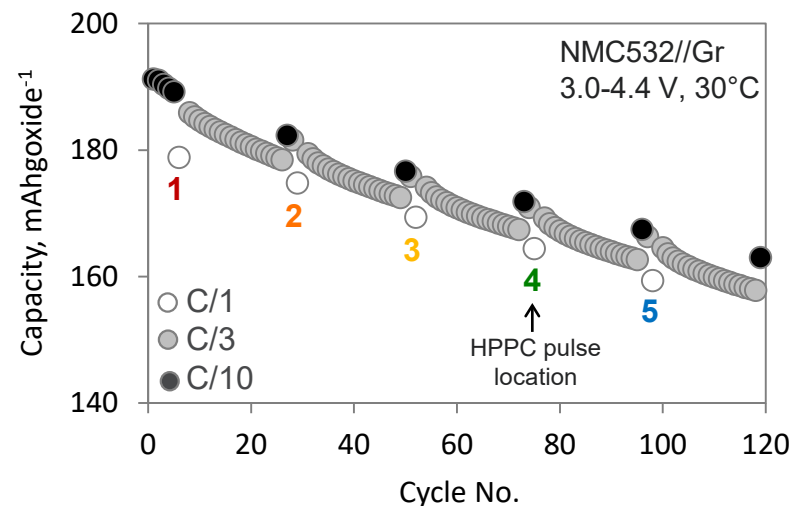
# Developed coin cell assembly and cycling protocols to enable comparison of data generated by team members

Protocol includes 3h hold at the UCV to accelerate aging



Protocol provides information on cell capacity and impedance changes

See also BAT252

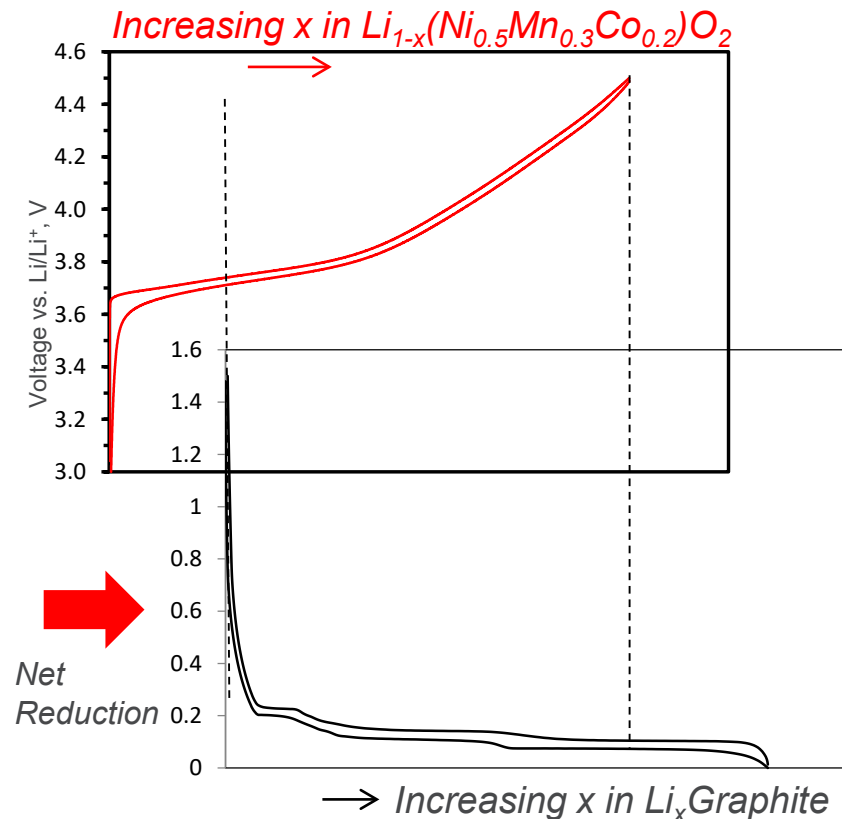


# Aging of cells with the baseline chemistry leads to capacity loss and impedance rise

**Protocol: 3–4.4 V w/3h hold at 4.4 V, 30 °C**

## Observations

- Positive electrode is main contributor to impedance rise
- Li-trapping in negative electrode SEI is main contributor to capacity fade
- Electrode potential window shifts observed on aging
  - Reduces utilization of electrode active material
  - Causes positive electrode to cycle at higher SOC

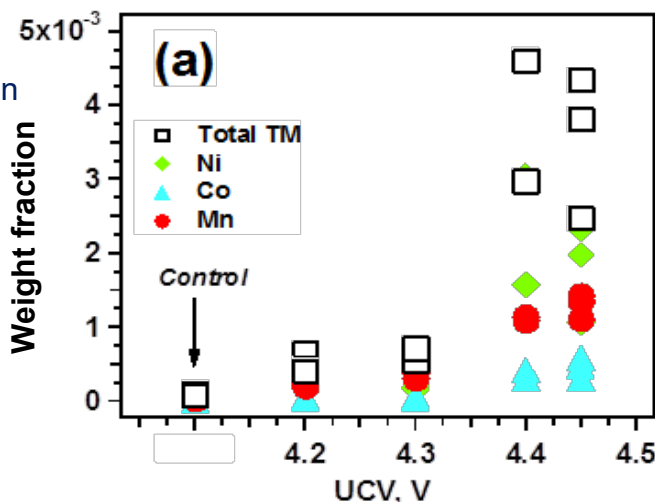


**Similar trends are observed in other layered oxide/graphite systems (e.g. NMC811/Gr, NMC622/Gr, NCA/Gr, etc.)**

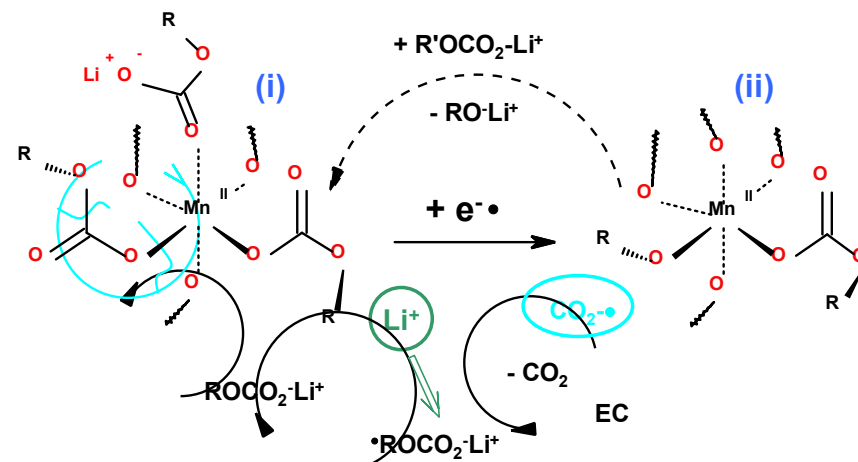
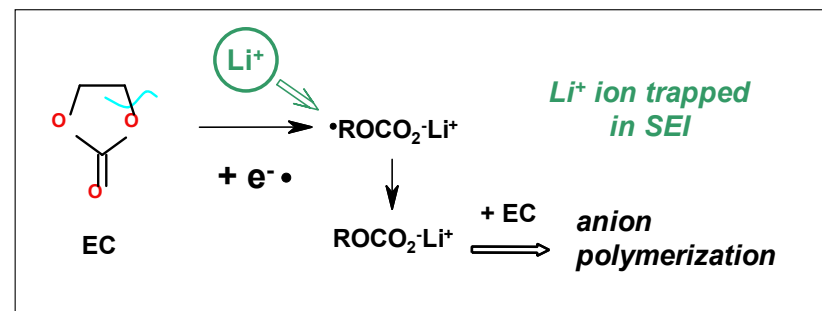
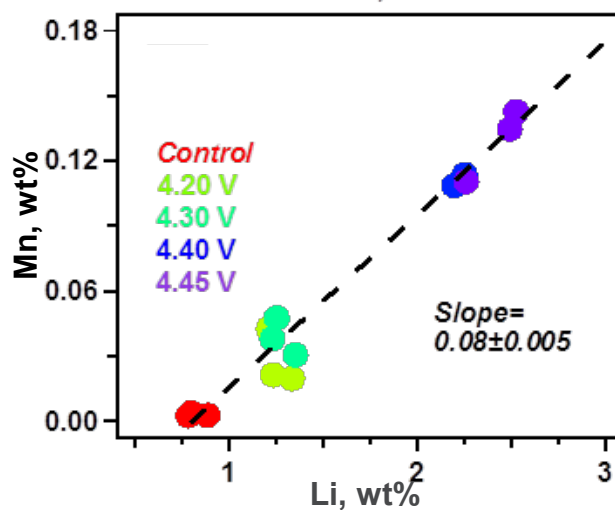
# Cell capacity fade is accelerated by the deposition of transition metal elements in the negative electrode

## Transition metal dissolution from oxide is increases with UCV

Higher TM content and greater variation at higher UCV



Correlation between Mn and Li content in negative electrode

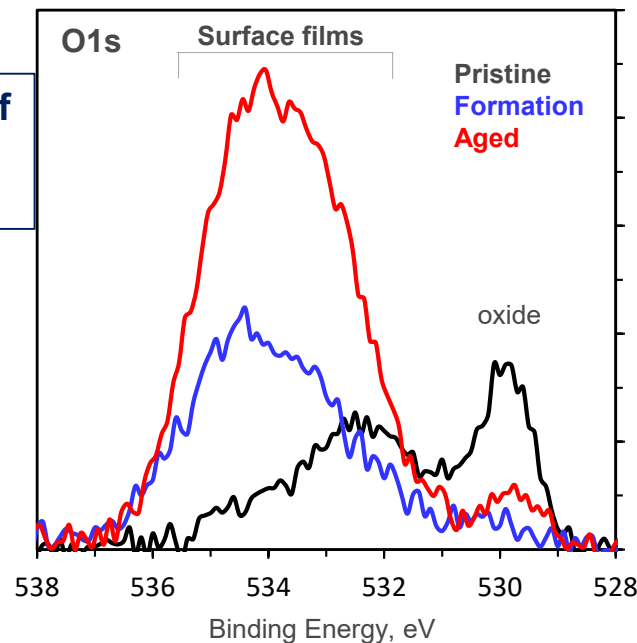
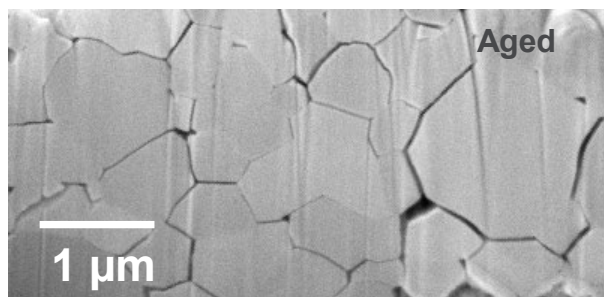
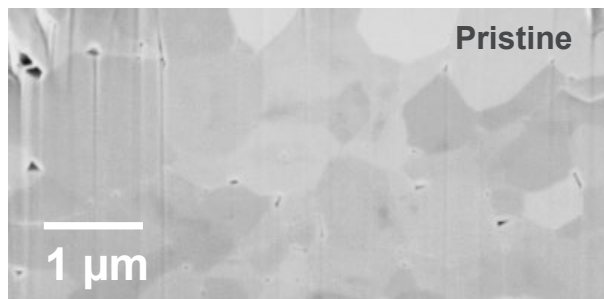


Mechanism proposed to explain effect of Mn ions in the SEI

# Impedance rise at positive electrode can be attributed to resistive surface films, particle isolation, etc.

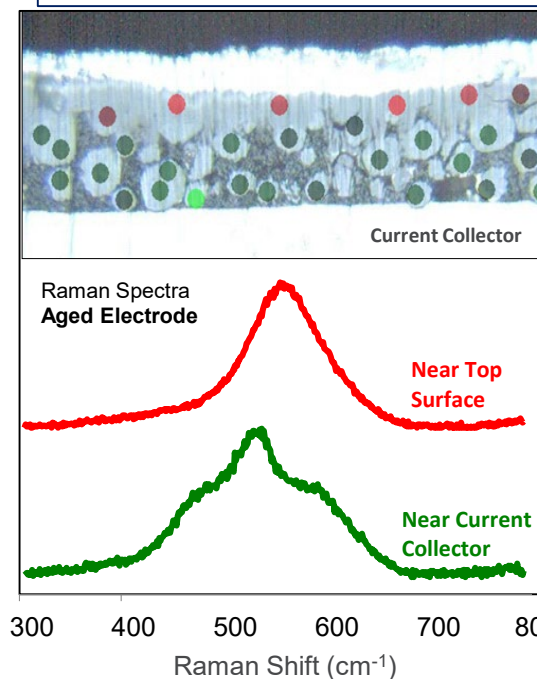
## Composition/impedance heterogeneity in electrode cross sections detected by Raman Spectroscopy

Aging increases the content of oxygen bearing species at the oxide-electrolyte interfaces



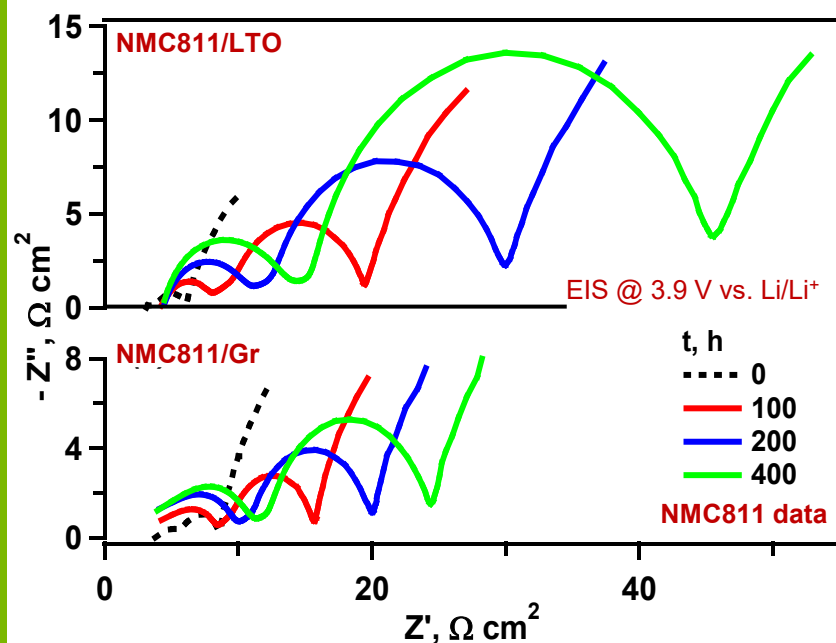
Primary particle separation (inter-granular cracking) evident in aged oxides

In an aged/discharged cell oxide particles near electrolyte interface have higher impedance



# Cathode impedance rise is accelerated by gases generated in cell during electrolyte oxidation reactions

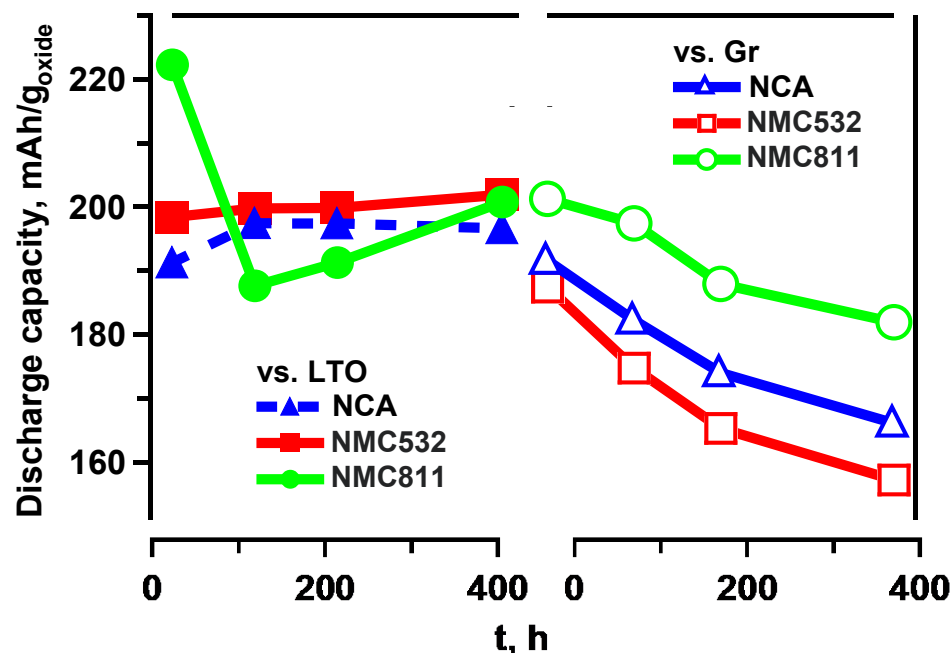
## Reactions at the graphite electrode reduce gas content in cells



**Cathode** impedance increase during aging is greater in LTO cells than in Gr cells. The increase is observed in both high-frequency arc (electron conduction pathway degradation, particle cracking, etc.) and mid-frequency arcs (Li<sup>+</sup> ion conduction at particle surfaces, etc.)

Calendar aging, Reference electrode cells  
NMC811 @ 4.48 V vs. Li/Li<sup>+</sup>, 30 °C

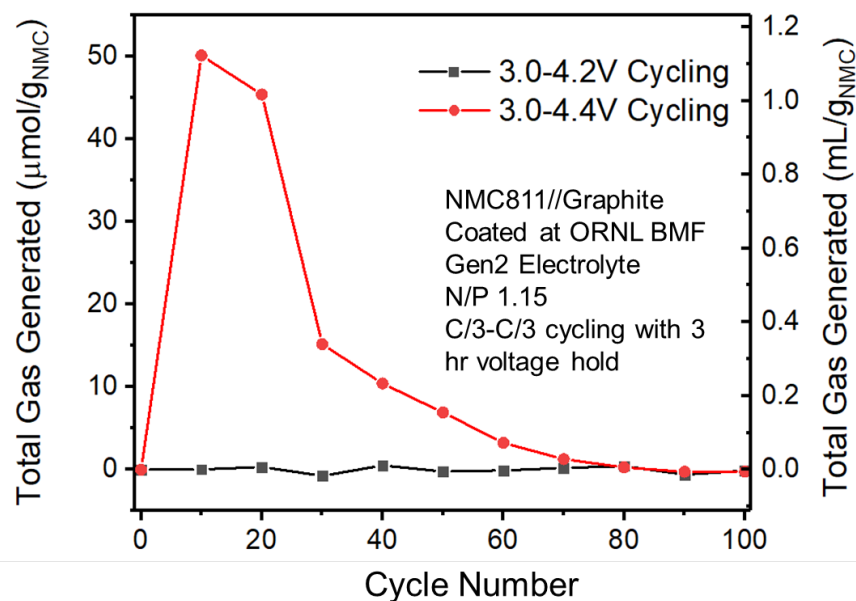
Li<sup>+</sup> inventory gains in LTO cells is a consequence of electrolyte oxidation. Gr cells also gain capacity, but this gain is masked by Li<sup>+</sup> ion inventory loss to SEI



# Significant gas evolution in pouch cells cycled at high voltage (NMC811//graphite)

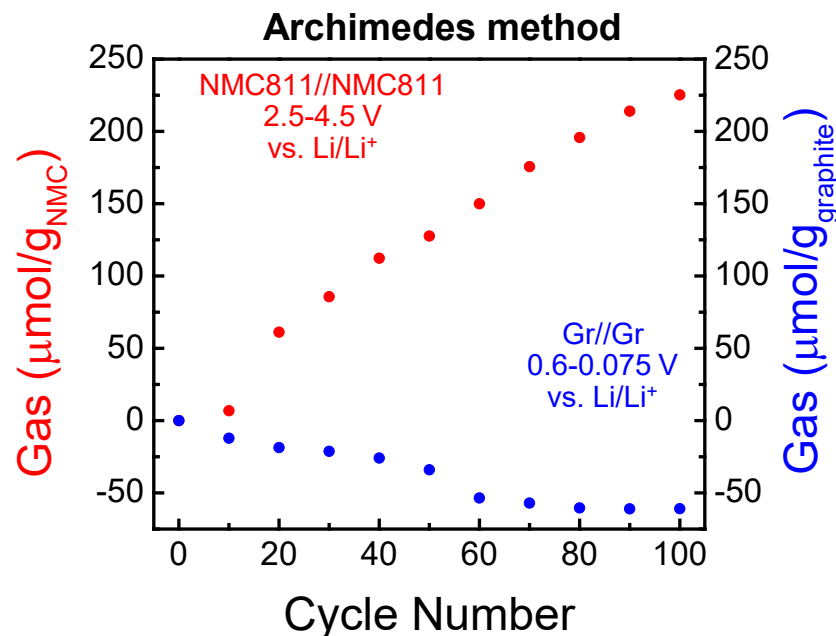
## Nickel-rich cathode mainly responsible for gas generation

Gas volume measured by the Archimedes method.  
Cycle 0 is after 4 formation cycles and degassing



Minimal gas generation in 3.0-4.2 V cycling window.  
 Significant gas generation in 3.0-4.4 V cycling window during the early cycles; gas depletion during the later cycles.

Symmetric Gr//Gr and NMC811//NMC811 cells



Continuous gas (e.g. CO<sub>2</sub>) generation in NMC-811 cell on cycling  
 Gas (e.g. CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) generated in Gr cell is consumed on cycling

# Electrolyte Sprints implemented to find possible solutions to performance degradation

## Ideal electrolyte additives and fluorinated solvents would

Prevent oxygen loss from oxide surface

“Neutralize” protic species generated at high voltages (from electrolyte oxidation reactions)

Form protective surface films on electrodes

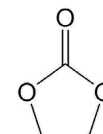
Anode additive	Structure
2,4,6-trivinylcyclotriboroxane (tVCBO)	
Prop-1-ene-1,3-sultone (PES)	
Phenyl boronic acid ethylene glycol ester (PBE)	
Lithium bis(oxalato)borate (LiBOB)	
Vinylene carbonate (VC)	

To minimize capacity fade

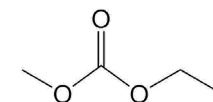
Cathode additive	Structure
Lithium difluoro(oxalate)borate (LiDFOB)	
Tris(trimethylsilyl) phosphite (TMSPi)	
Triethyl phosphite (TEPi)	

To minimize impedance rise

Gen2 solvents

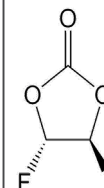


30%

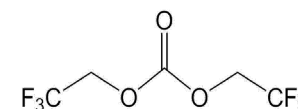


70%

FE-3 solvents



30%



70%

# Figure of merit (FOM) methodology developed to identify promising electrolyte formulations

Numerical values allows easier comparison between various electrolytes

## FOM-E

### Anode additives

**Baseline**  
170

LiBOB PBE PES tVCBO VC

Cathode additives

LiDFOB	123	89	128	111	110
TEPi	116	84	78	97	147
TMSPi	115	169	154	204	200

Better

Baseline

Worse

**FOM-E:** Number of cycles it takes until 80% of baseline energy density (Wh/kg<sub>oxide</sub>) reached. Only the tVCBO + TMSPi and VC + TMSPi additive combinations have an FOM-E better than that of the baseline electrolyte

Additive compounds in baseline Gen 2 electrolyte

**FOM-P:** Number of cycles it takes until 80% of baseline power density (mW/cm<sup>2</sup>) reached. Several electrolytes with TMSPi have FOM-P better than that of the baseline electrolyte

## FOM-P

### Anode additives

**Baseline**  
23

LiBOB PBE PES tVCBO VC

Cathode additives

LiDFOB	10	116	18	30	29
TEPi	54	16	5	23	23
TMSPi	99	113	22	133	31

Better

Baseline

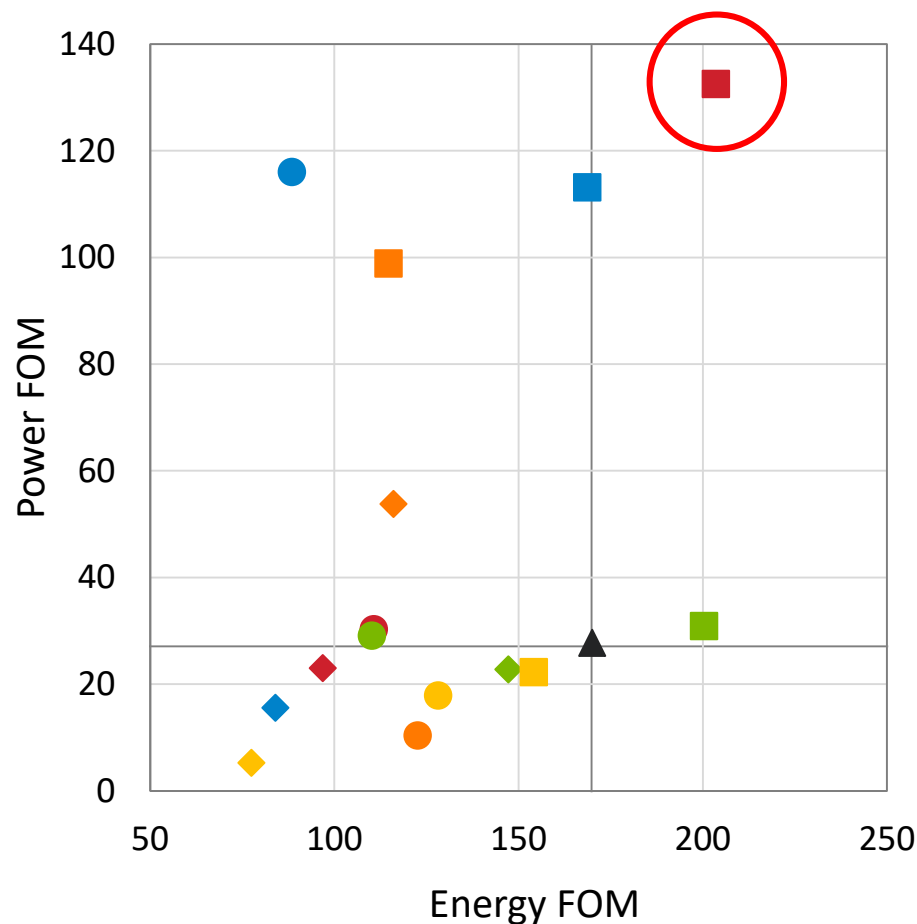
Worse

# Energy FOM vs. Power FOM

Cells with (0.25 wt% tVCBO + 1 wt% TMSPi) added to the baseline electrolyte have the best Energy FOM and Power FOM

Anode	Cathode
VC	LiDFOB ○
PES	TMSPi □
LiBOB	TEPi ◇
PBE	
tVCBO	

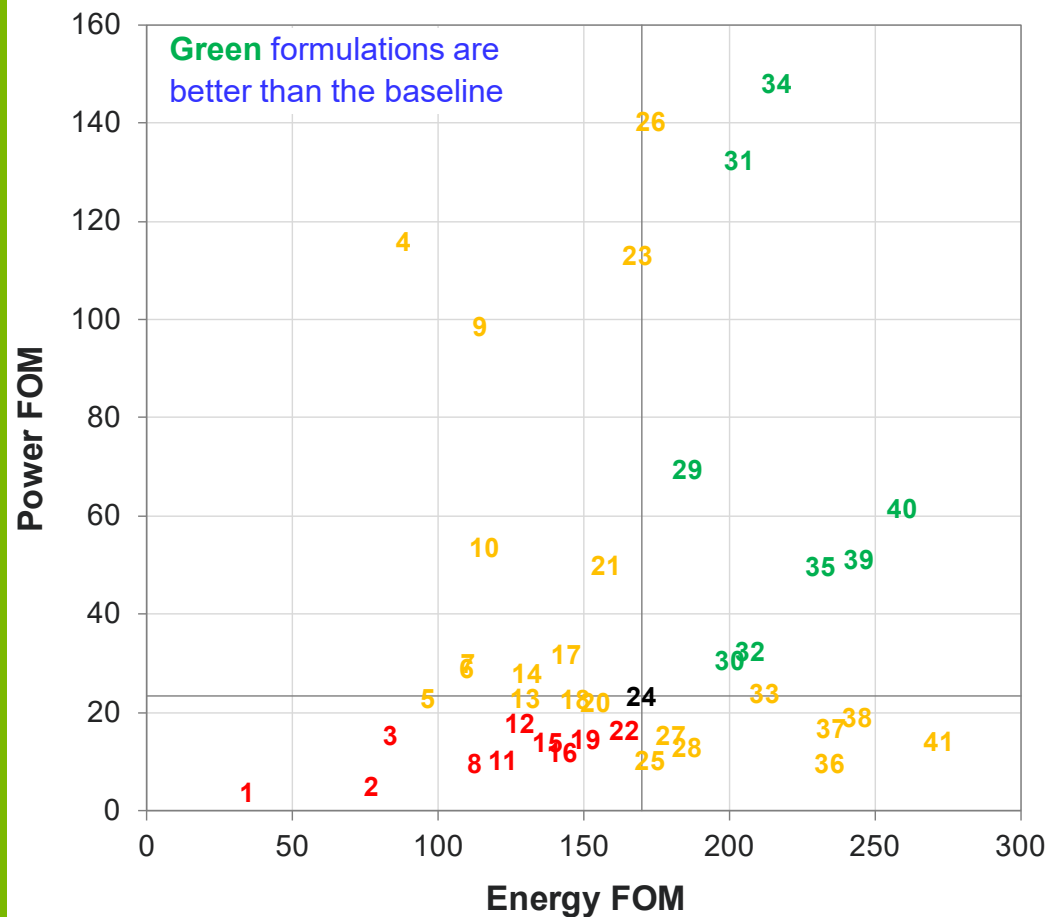
- Energy + Power	+ Energy + Power
- Energy - Power	+ Energy - Power



- tVCBO & TMSPi ■
- VC & TMSPi ■
- Baseline ▲
- PBE & TMSPi ■
- PES & TMSPi ■
- VC & TEPi ◆
- PES & LiDFOB ●
- LiBOB & LiDFOB ●
- LiBOB & TEPi ◆
- LiBOB & TMSPi ■
- tVCBO & LiDFOB ●
- VC & LiDFOB ●
- tVCBO & TEPi ◆
- PBE & LiDFOB ●
- PBE & TEPi ◆
- PES & TEPi ◆

# Energy FOM vs. Power FOM

Information can help identify relevant questions that need answers

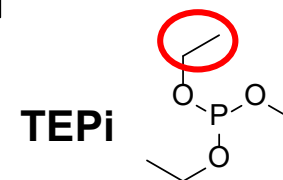
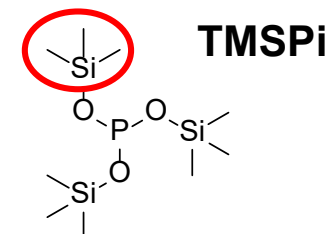
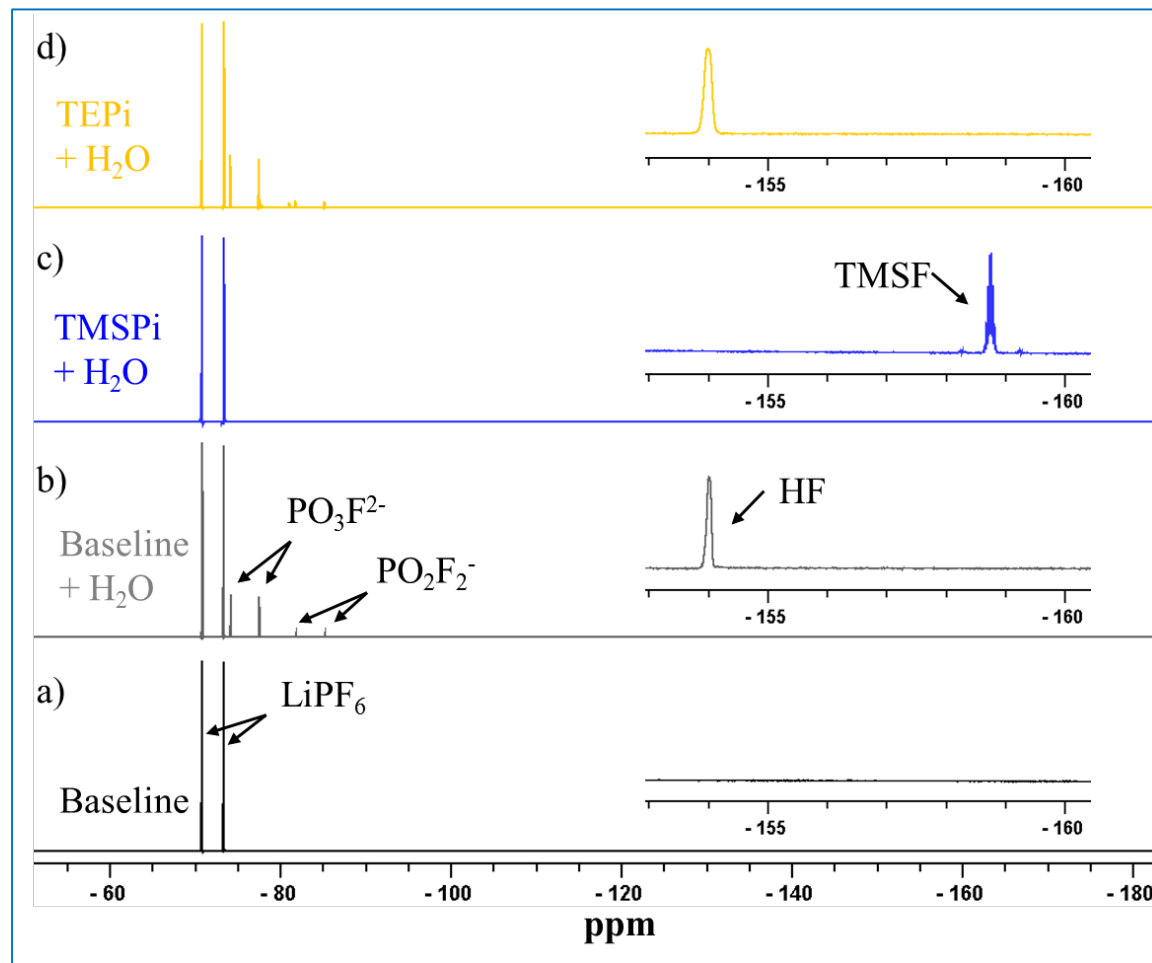


Label	Formulation	Label	Formulation
24	Baseline	41	0.5 VC & 1.0 TMSPa
40	1.0 VC & 1.0 TMSPi	38	1.0 TMSPi (2 wk old)
39	0.5 VC & 1.0 TMSPi	37	1.0 TMSPa
35	Lit Sep + 1.0 TMSPi (1 wk old)	36	1.0 TMSPi (3 wk old)
34	1.0 TMSPi (1 wk old)	33	2.0 FEC & 1.0 TMSPi (1 wk old)
32	1.0 TMSPi	28	1.0 VC & 2.0 TMSPi
31	0.2 tVCBO & 1.0 TMSPi	27	1.0 VC & 1.0 TMSPi (1 wk old)
30	2.0 VC & 1.0 TMSPi	26	0.25 tVCBO & 1.0 TMSPi (symm)
29	0.5 VC & 1.0 TMSPi & 0.5 TEPI	25	10.0 TMSPi (1 wk old)
22	Lit Sep	23	0.25 PBE & 1.0 TMSPi
19	1.0 VC & 0.5 TMSPi	21	0.25 tVCBO
16	0.5 TMSB	20	1.0 PES & 1.0 TMSPi
15	1.0 TEPI	18	2.0 VC & 1.0 TEPI
12	2.0 PES & 1.0 LiDFOB	17	2.0 VC & 1.0 TMSPi & 1.0 DME
11	1.0 LiBOB & 2.0 LiDFOB	14	1.0 VC
8	1.0 TMSB	13	1.0 VC & 1.0 TEPI
3	0.25 PBE & 1.0 TEPI	10	1.0 LiBOB & 1.0 TEPI
2	1.0 PES & 1.0 TEPI	9	1.0 LiBOB & 1.0 TMSPi
1	0.3 PCl3	7	0.25 tVCBO & 2.0 LiDFOB
		6	2.0 VC & 2.0 LiDFOB
		5	0.25 tVCBO & 1.0 TEPI
		4	0.25 PBE & 2.0 LiDFOB

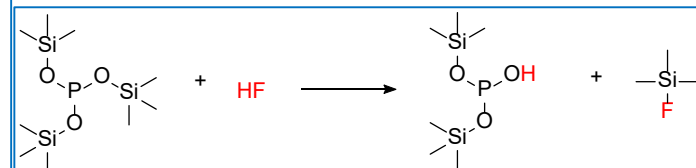
- Why is TMSPi (32) better than TEPI (15)?
- Why does the 1wk aged TMSPi (34) show the highest Power FOM?

# TMSPi (but not TEPi) is able to scavenge HF from electrolyte solutions

Water added to Baseline (Gen2) electrolyte to generate HF



$^{19}\text{F}$  NMR spectra



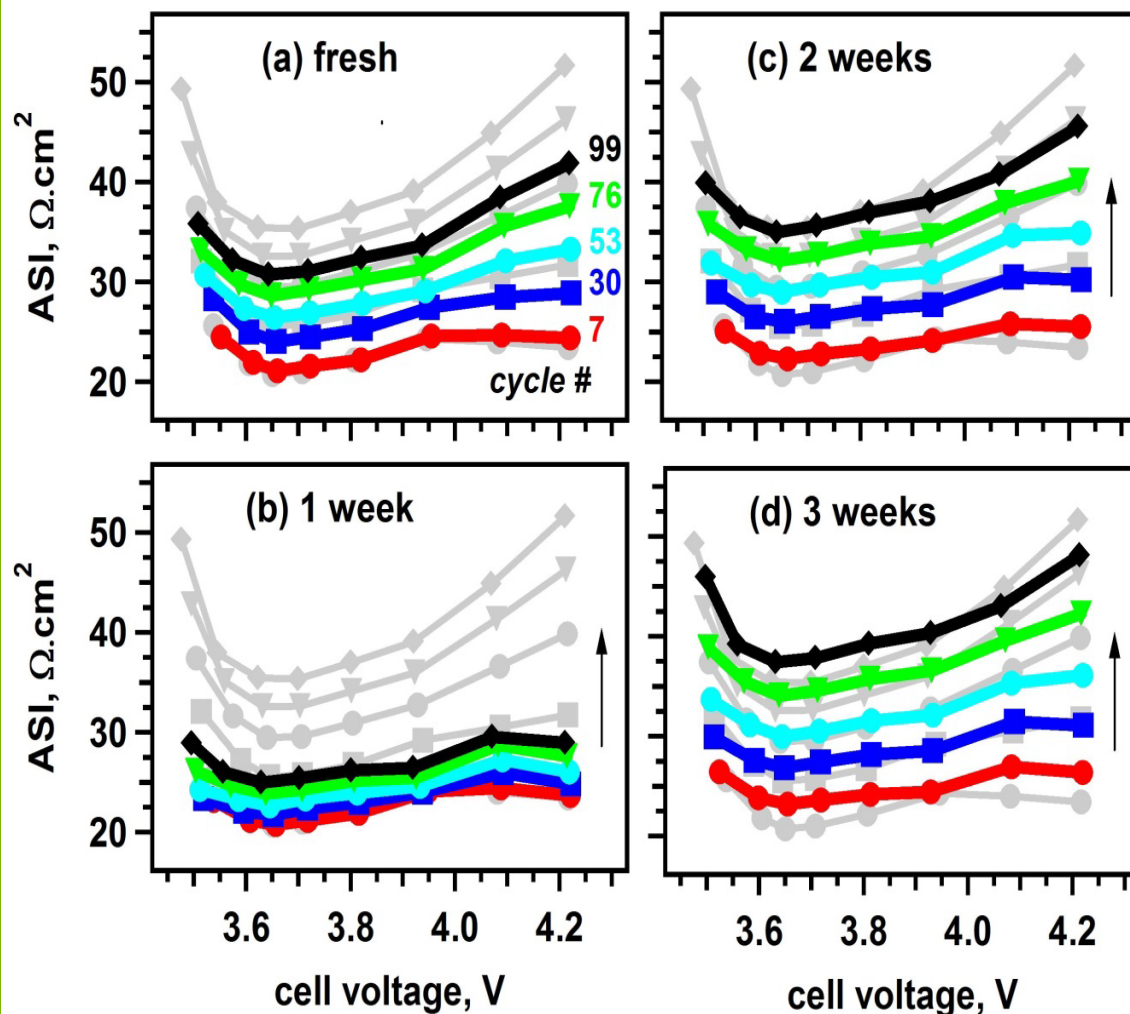
$\text{LiPF}_6$  hydrolysis species are generated when water is added to the baseline electrolyte.

These species are also observed in solutions containing TEPi.

These species are **not** observed in solutions with TMSPi. Instead TMSF is observed (reaction with HF shown above).

# Cell performance improves after electrolyte is aged

## Lowest impedance rise for cells with “1-week old” electrolyte

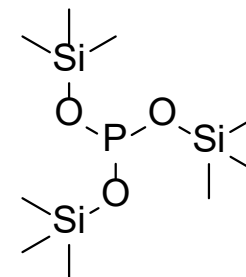


NMC/532/Gr cells

Electrolyte: Gen 2 w/ 1 wt% TMSPi

(aged for various periods)

3-4.4 V w/ 3h hold at 4.4 V



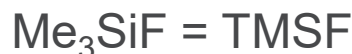
Additives can react with the baseline electrolyte to form compounds that have beneficial or detrimental effects on cell life

# The TMSPi molecule itself is not involved directly in forming protection films on the oxide surface

The active component,  $\text{PF}_2\text{OSiMe}_3$ , forms as lithium salt in the electrolyte reacts with TMSPI



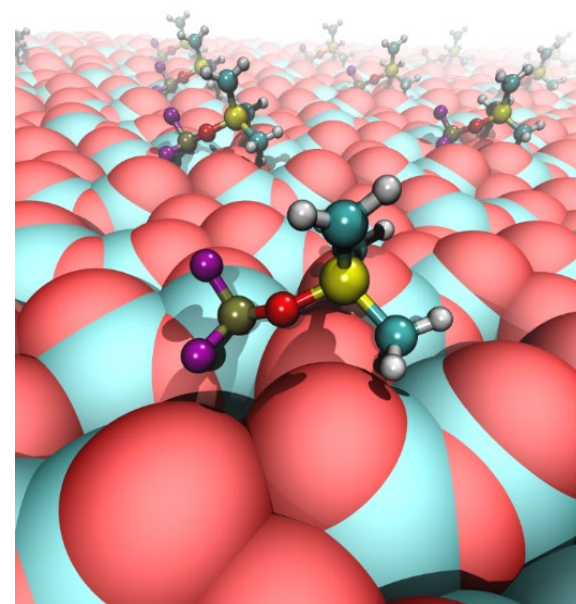
Starting material



Only these two compounds are present in solution after 1 week of aging

Proposed Mechanism - based on experimental observations and computational studies

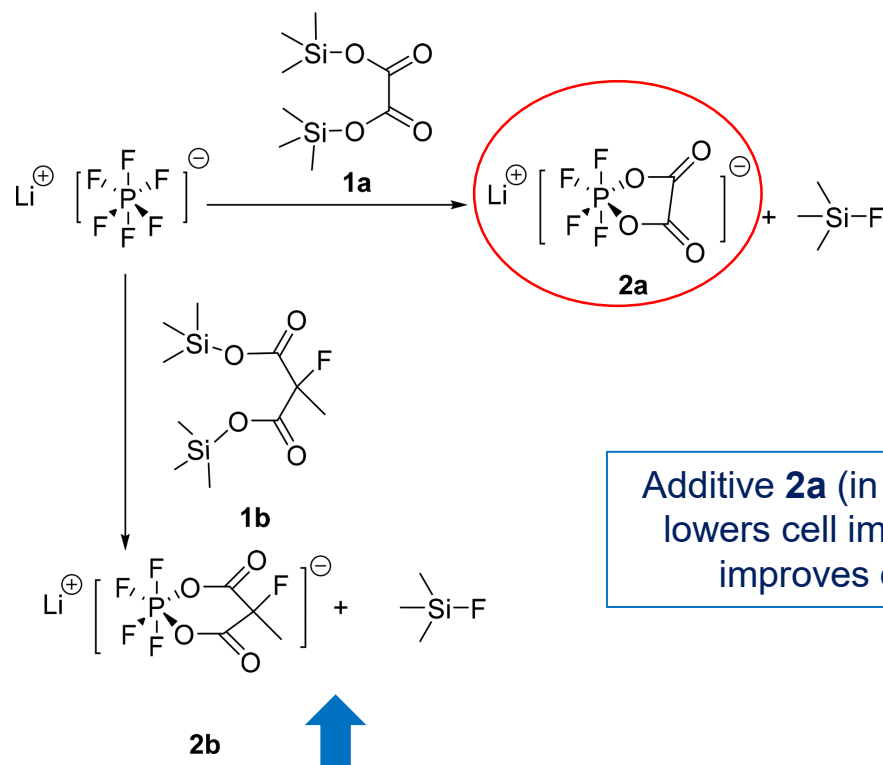
- Physisorption of  $\text{PF}_2\text{OSiMe}_3$  on oxide.  $\text{PF}_2\text{OSiMe}_3$  makes a bond with TM ion leaving behind a vacancy.
- $\text{PF}_2\text{OSiMe}_3$  reacts with  $\text{PF}_6^-$  and transforms to  $\text{PF}_5\text{OP}(\text{F}_2)$ . There is O-F exchange between the  $\text{PF}_5\text{OP}(\text{F}_2)$  and the oxide surface leading to formation of  $\text{OPF}_2\text{-O-PF}_2\text{O}$ , which caps the TM ion catalytic center, thus preventing further oxidation of the solvent.



$\text{PF}_2\text{OSiMe}_3$  molecules binding to reaction centers on the oxide particle surface. For the ball-and-stick molecules attached to cathode surface, olive green indicates phosphorus (P); purple, fluorine (F); red, oxygen (O); gold, silicon (Si); structure above Si is the methyl group ( $\text{CH}_3$ ).

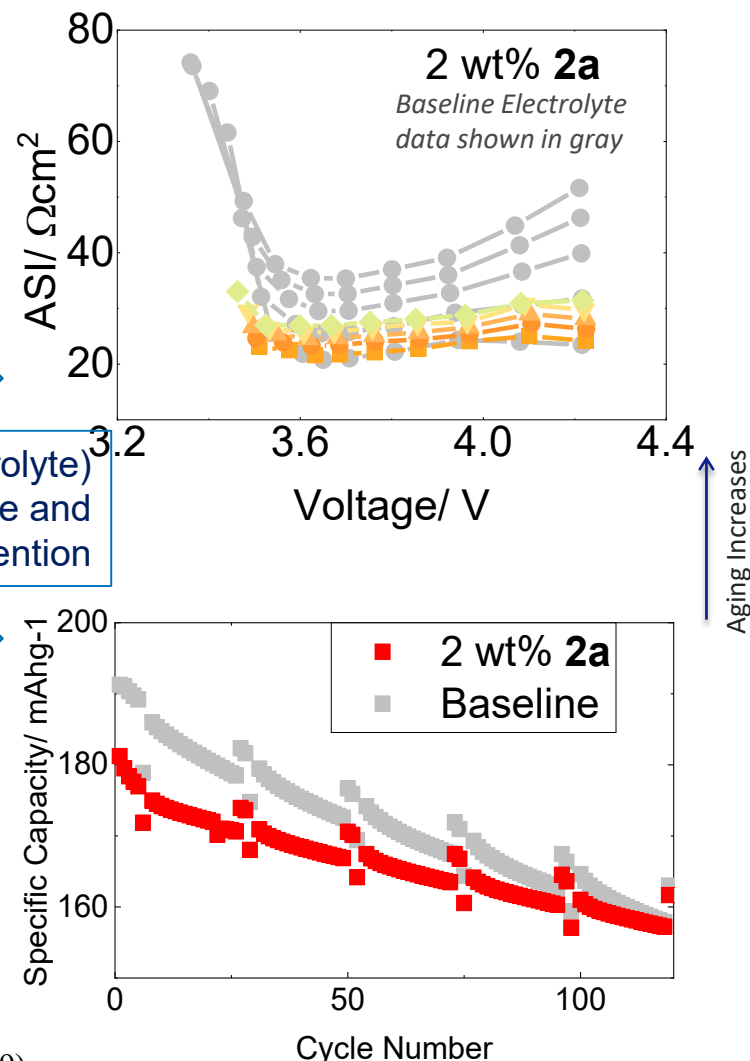
# “In situ” synthesis of Moisture Sensitive Additives

Additives are formed through reactions with the electrolyte salt



Additive **2a** (in Gen2 electrolyte) lowers cell impedance rise and improves capacity retention

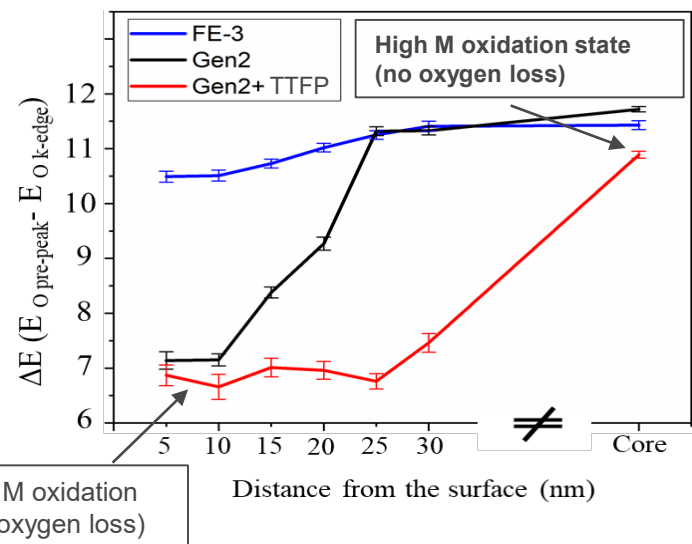
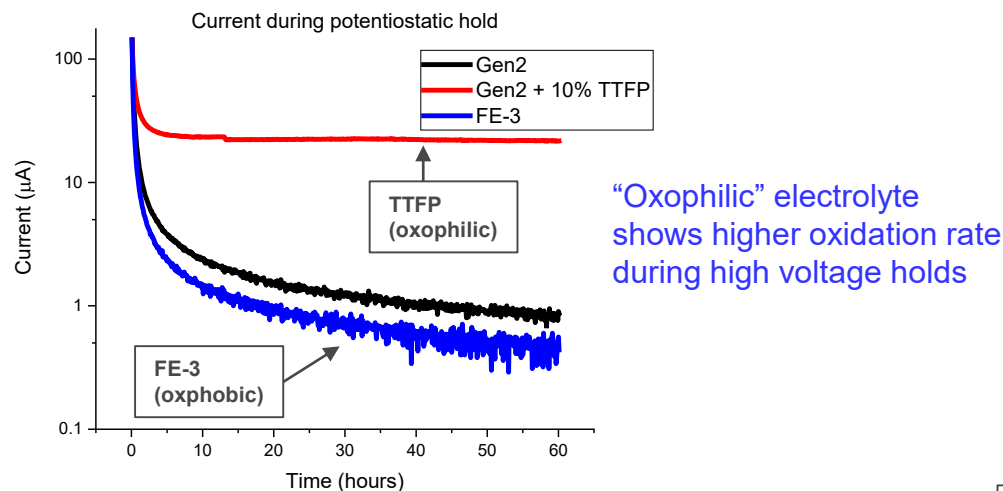
In situ syntheses of two electrolyte additives 2a and 2b through bidentate monoaddition of bis-trimethylsilyl diesters to the  $\text{PF}_6^-$  anion in carbonate solvents. These reactions proceed with almost 100% efficiency at room temperature.



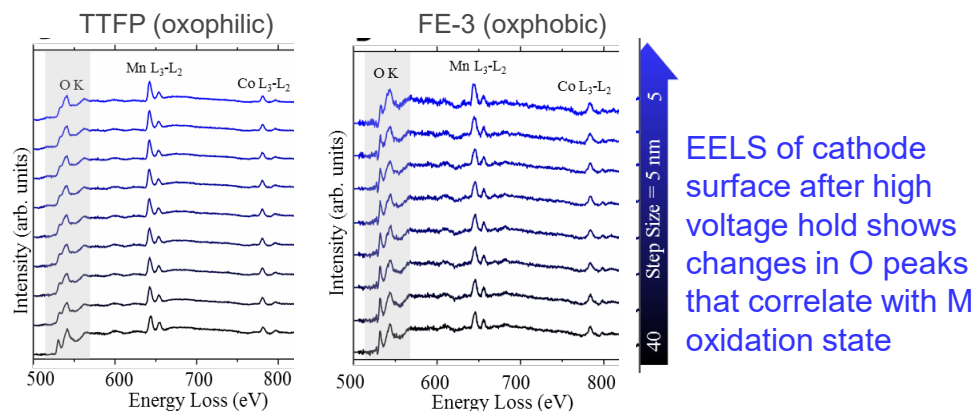
C. Liao et al. US Patent Application No. 16/175,497 (2019)

# Fluorinated electrolytes lower rate of electrolyte oxidation

“Oxophilic” components increase oxygen loss and rock-salt behavior, “oxophobic” components limit degradation. Oxygen loss manifests as a higher oxidation current.



## EELS on cycled cathode



Oxophilic electrolytes show high decomposition currents and cause substantial oxygen loss from the oxide surface (~25 nm degradation layer). Oxophobic (fluorinated) electrolytes show less surface degradation and lower rates of electrolyte oxidation.

See also BAT252

# Summary

- Developed coin cell assembly and cell cycling protocols to enable comparison of data generated by various team members
  - Information has been published and feedback from the battery community has been very positive
- Demonstrated that the causes of performance degradation in various layered oxide-graphite systems (NMC532/Gr, NMC811/Gr, NCA/Gr, etc.) are similar
  - The positive electrode is main contributor to cell impedance rise and Li loss in the graphite negative is mainly responsible for capacity fade
- Showed that electrode crosstalk plays an important role in degradation of cell performance
  - Developed mechanisms to explain the detrimental effect of Mn ions in the graphite SEI
- Revealed that the accumulation of gases (generated at the positive electrode during high voltage cycling) increases cell impedance rise
  - Combination of electrolyte oxidation at high (layered-oxide) potentials and electrolyte-reduction at low (lithiated-graphite) potentials can lead to electrolyte depletion, which can severely degrade cell performance and life
- Developed Energy and Power Figure of Merit (FOM) criteria and identified electrolyte additive combinations that outperformed the baseline (Gen2) electrolyte
  - Used the FOM criteria to define questions for detailed study of interfacial mechanisms
- Demonstrated that additive compounds can be altered by reactions with the electrolyte
  - Some reaction products mitigate cell performance loss, while others accelerate degradation
- Concept of additive reactions with electrolyte has been used to for *insitu* synthesis of compounds that are otherwise difficult to prepare
  - Some of these *insitu* synthesized compounds have beneficial effects on cell performance and life

# Future Work

## Concepts and ideas developed during project can be applied to next-gen cathode program

- Standardization of cell assembly and cycling protocols is important
  - Protocols for new program are based on “lessons learned”
- Figure-of-Merit criteria can be used to compare performance of the Next-Gen layered-oxide compounds under development
  - Energy and Power Performance are common themes for transportation
- Cell performance degradation can be studied with the various diagnostic tools and methodologies developed in the project
  - Electrochemical (3-electrode cells, symmetric cells) and physicochemical (XRD, HR-TEM, XAS, gas analysis, etc.) techniques will continue to guide the selection of electrode and electrolyte materials for high-performance cells
- Computational methodologies will continue to provide information on materials and mechanisms
  - Physicochemical models can be used to examine the effect of electrode and cell parameters and atomistic models can be applied to examine/explain mechanisms/process at the electrode/electrolyte interfaces

# Response to Previous Year Reviewers' Comments

**Three reviewers commented on our presentation. We are grateful for their thoughtful comments. Selected excerpts are given below.**

- The reviewers' comments were generally positive.
  - “project is very important and extremely relevant to DOE objectives”
  - “proceeds in a logical manner with a wide array of characterization techniques”
  - “excellent strides toward understanding of electrolyte additive function”
  - “great insights to understand interfacial reactions between electrolyte and electrode”
- One reviewer indicated that “it would be particularly desirable to share the protocol for determining these figures of merit (FOMs) with the community to standardize such evaluations.” We agree. Our work has been published in the open literature and the protocol/methodologies are available to the community.
- Another reviewer noted that more fundamental surface studies needs to be done in understanding electrolyte additive mechanisms. We agree. During the past fiscal year, through closely coupled fundamental science experiments and computational models we revealed that it is not the TMSPi additive that protects the oxide surface, but rather a derivate ( $\text{PF}_2\text{OSiMe}_3$ ) formed by reactions of the compound with the electrolyte salt. These reactions leads to the gradual replacement of the TMS groups with F.
- Another reviewer suggested that we examine the evolution of the electrode/electrolyte interfaces with techniques such as high-resolution transmission electron microscopy. We did use HRTEM and EELS techniques to determine that oxides cycled in oxophobic (fluorinated) electrolytes release less oxygen and show minimal surface degradation.

# Publications and Presentations

- Fulya Dogan, J. - S. Park, J. Croy, B. Key, J. T. Vaughey “Investigation of Aluminum Environments in  $\text{Al}_2\text{O}_3$  coated cathodes: The Effect of Cathode Composition on Electrochemical Performance and Aluminum Local Environments” Gordon Conference on Batteries, Ventura, CA, February 2016.
- A. Hubaud, F. Dogan, C. Pebbles, C. Liao, J. Vaughey “Interfacial Stability of Ni-rich Layered Oxide Cathodes” IBA2016, Nantes, France, March 2016.
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- Hakim Iddir, “Atomistic Models of High-capacity Layered Metal Oxide Cathode Materials”, Argonne National Laboratory. February 16th, 2017 (invited talk) . AIChE Chicago February 2017 Meeting and Tour.
- Hakim Iddir, Condensed Matter/Biological Physics Seminar UIC. March 9, 2017 (invited talk), “Atomistic models of high-capacity layered metal oxide cathode materials”
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- 10<sup>th</sup> Annual AIChE Midwest regional Meeting. Chicago, IL Transition Metal Segregation and Phase Transformations on the Surfaces of Layered  $\text{Li}(\text{Ni}_{1-x-y}\text{MnxCoy})\text{O}_2$  (NMC) Cathode Materials for Li-ion Batteries
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# CONTRIBUTORS AND ACKNOWLEDGMENT

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- Materials Engineering Research Facility (MERF)
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## High-Energy/Voltage Project Contributors

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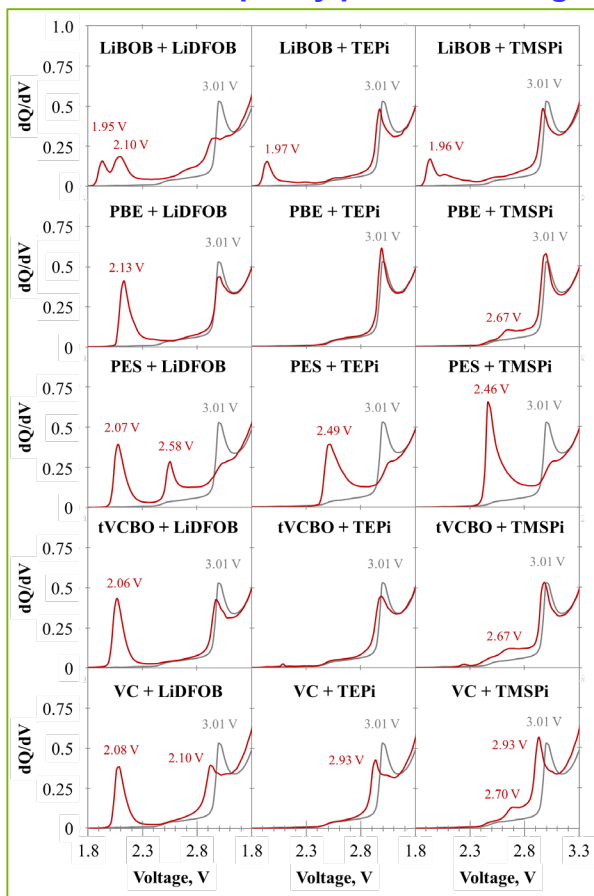
# TECHNICAL BACKUP SLIDES

**[maximum of five]. These back-up technical slides will be available for your presentation and will be included in the web PDF files released to the public.)**

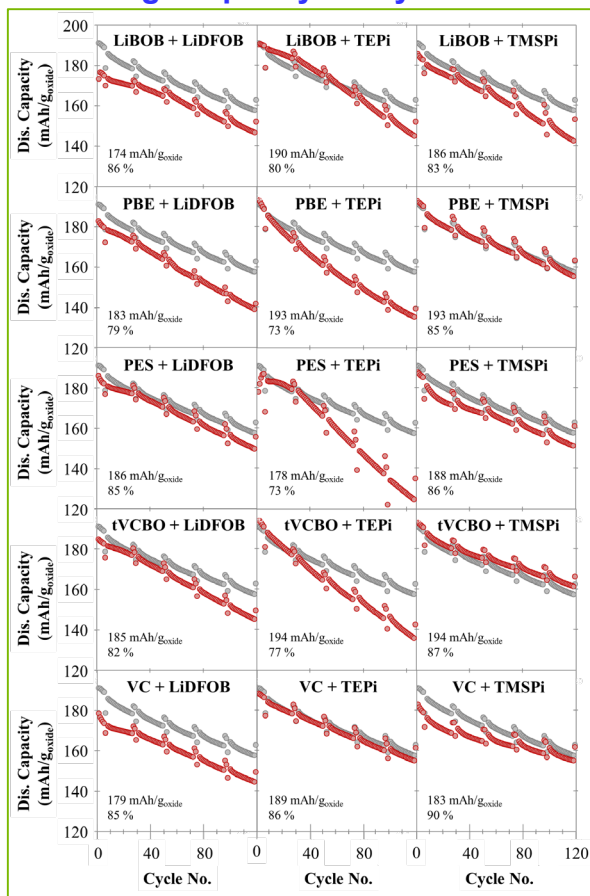
# Electrolyte additives alter cell performance

Large datasets generated even from testing 16 different electrolyte chemistries. How to identify chemistries that outperform the baseline?

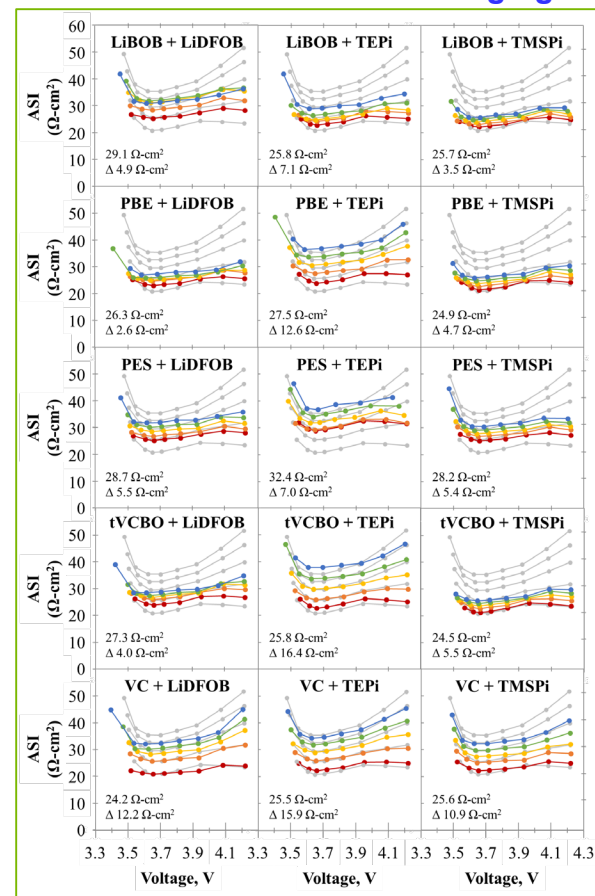
Differential capacity plots: 1<sup>st</sup> charge



Discharge capacity vs. cycle number

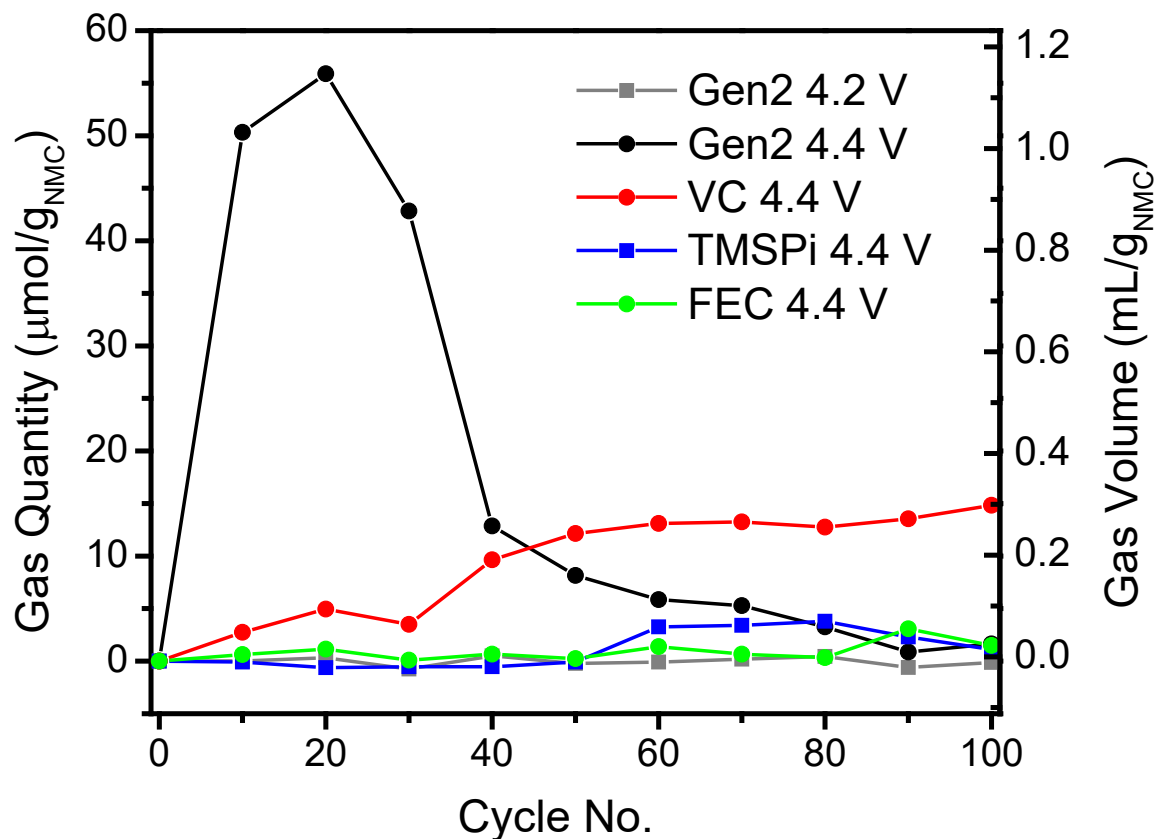


ASI vs. V as a function of aging



Gen2 electrolyte (EC:EMC (3:7 w/w) + 1.2 M LiPF<sub>6</sub>) data shown in grey in all plots

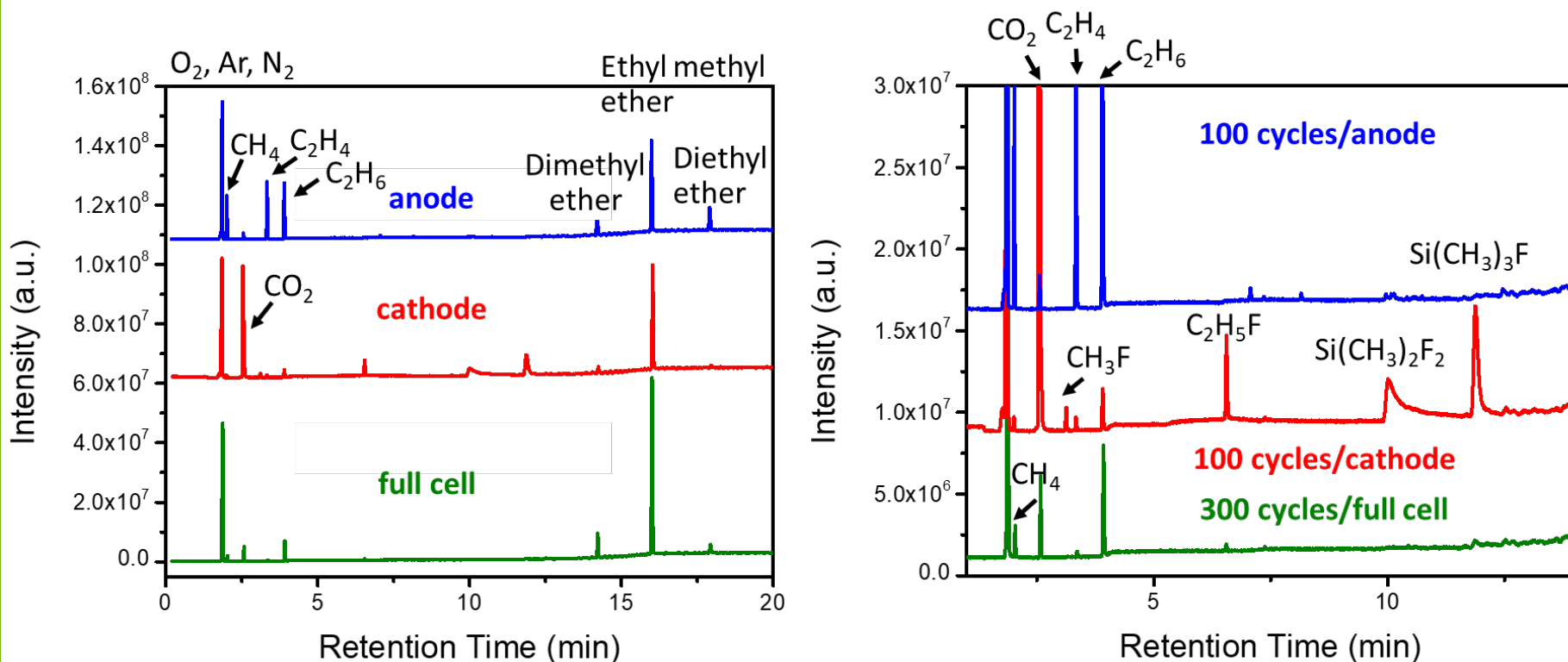
# Electrolyte additives alter gas evolution behavior



All additives suppressed initial spike in gas generation  
Cells with 2 wt.% VC show gradual rise in gas volume

# Symmetric cells contain gases not observed in full cells

## GC-MS of symmetric Gr//Gr and NMC811//NMC811 pouch cells provides evidence for cross-talk.

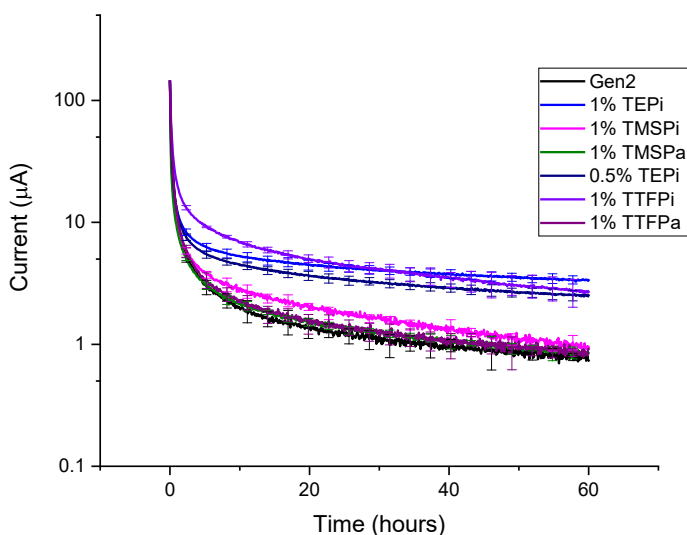


- Alkenes generated at the anode react at the cathode.
- CO<sub>2</sub> and fluorocarbons generated at the cathode react at the anode.

# Additive family and substituent group influences electrode interactions

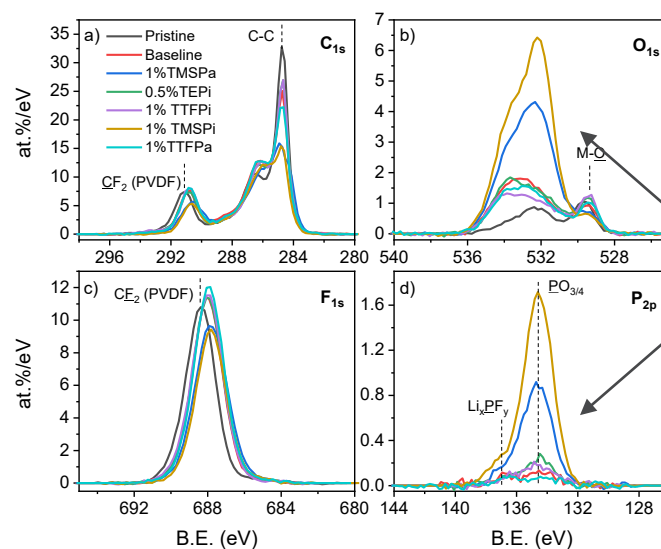
**TMS groups form surface layers on cathode (unlike ethyl and triethyl groups), phosphites have tendency to be oxidized at high voltage**

Influence of phosphite/phosphate additive on oxidation current during potentiostatic hold



Phosphates have lower oxidation currents than phosphites (phosphites can be oxidized)  
TMSPi has lower current than other phosphites.

Influence of phosphite/phosphate additive surface atomic environment (XPS) after hold



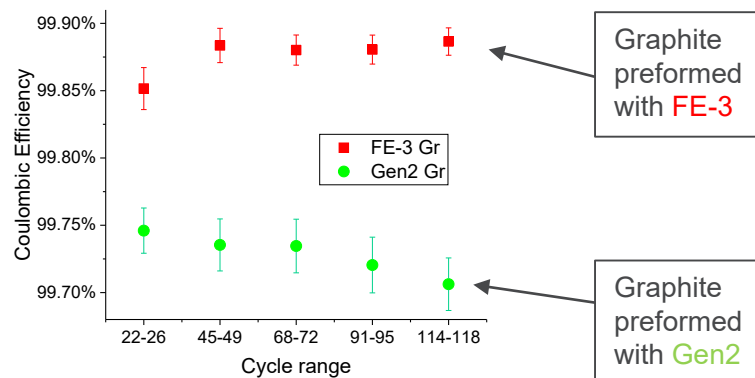
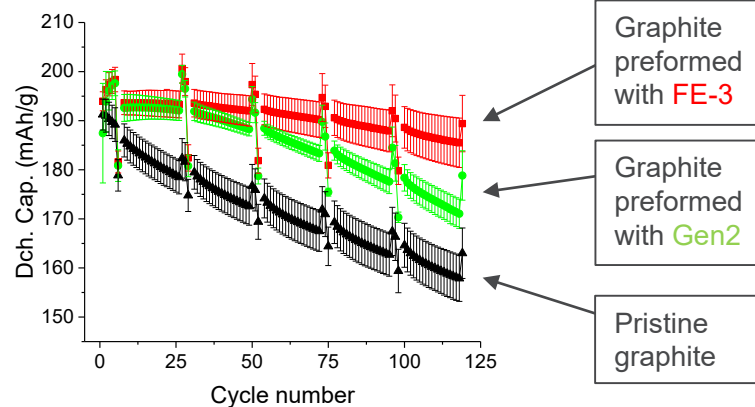
TMSPi and TMSPa show substantial O and P enrichment over ethyl and fluoroethyl substituent additives on cathode surface.

TMSPi forms a P and O rich film on the surface, and has a lower oxidation rate than other phosphites.

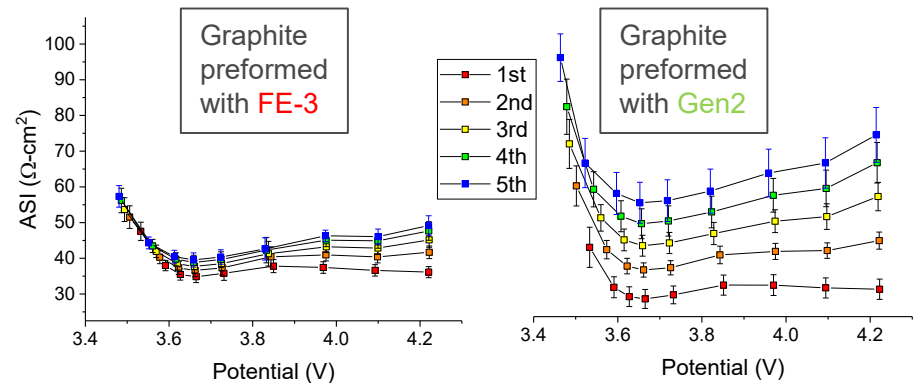
# Graphite preformed with FE-3 enhances baseline electrolyte performance

Baseline Gen2 electrolyte shows better stability in both cycling and impedance rise when paired with FE-3 preformed graphite

Influence of preforming electrolyte identity on capacity retention and coulombic efficiency



Influence of preforming electrolyte identity on impedance rise



Graphite preformed with FE-3 (FE-3 SEI) shows substantially better capacity retention and lower impedance rise

Anode SEI influence on impedance rise (cathode/electrolyte interface) indicates crosstalk is a contributor to impedance rise